Cyclobutadiene Epoxide

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Summary The isolation of a new cyclobutadiene epoxide is described

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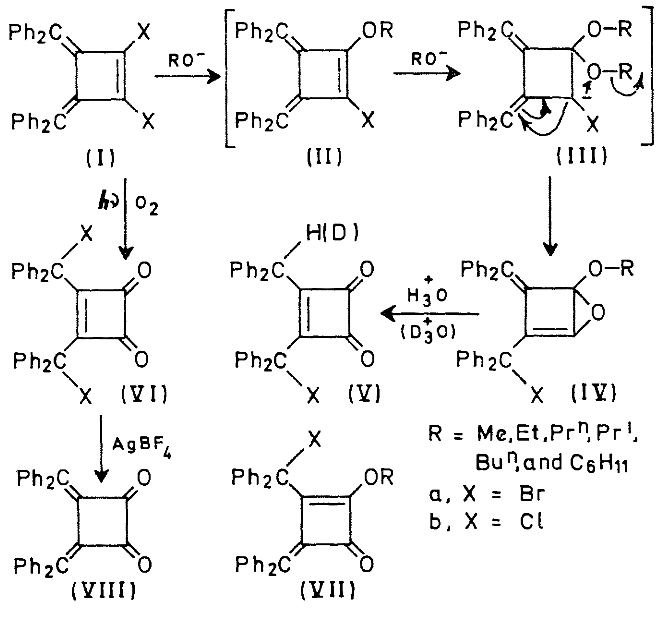
RECENTLY, we reported the reduction[1] of 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobutene (I) with sodium borohydride to afford 1-bromo-3,4-bis(diphenylmethylene)-cyclobutene *via* the dihydro-compound, 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobutane, and the photo-oxidation[2] of (I) to afford 3,4-bis(bromodiphenylmethyl)cyclobutene-1,2-dione (VI) The interesting reactivities of the *endo*-double bond of (I) prompted us to investigate the reaction of (I) with potassium alkoxide to give a new cyclobutadiene epoxide (IV) This is the first example of a cyclobutadiene epoxide, although cyclobutene epoxide[3] and episulphide[4] are known We describe the isolation and characterization of (IV), and 3-bromodiphenyl-4-diphenylmethylcyclobutene-1,2-dione (V) which was derived from (IV)



SCHEME

Heating a mixture of (I), alcohol, tetrahydrofuran dried over sodium, and potassium hydroxide (or sodium alkoxide) under reflux for 30 min, afforded the cyclobutadiene epoxide (IV) as colourless crystals in quantitative yield Methyl, ethyl, n-propyl, isopropyl, n-butyl, and cyclohexyl alcohols afforded the corresponding epoxide, but t-butyl and benzyl alcohols did not

All of the epoxides showed satisfactory analytical and spectral data Two characteristic i r bands of (IV) appeared at 1670 (w) and 1580 cm^{-1} (vs) regions Spectral data, for example, of the bromo-isopropyl derivative (IVa, R = Pr^i) [m p 186—188° (decomp)] were λ_{max} ($CHCl_3$) 281 (ϵ 32 300) and 315 nm(sh) (24,300), ν_{max} ($CHCl_3$) 1675 (*exo*-C=C), 1580 and 1570 (unsplit doublet, *endo*-C=C), 1260, 920 and 910 (unsplit doublet) and 840 (epoxide), and 1105 cm^{-1} (C–O), n m r ($CDCl_3$) τ 2 66 (d, C_6H_5, 10H), 3 18 (m, C_6H_5, 10H), 4·98 (q, J6 Hz, C*H*, 1H), and 8 99 (d, J6 Hz, CH_3, 6H) It is reasonable to assign the bands at 1670 and 1580 cm^{-1} to the stretchings of *exo*- and *endo*-double bonds, respectively, since (Ia) and (Ib) absorbed at 1655 and 1510, and 1660 and 1530 cm^{-1}, respectively, and since ν(C=C) of the *endo*-double bond of (V) and (VI) appeared at 1545 and 1535 (unsplit doublet) and 1540 cm^{-1}, respectively

The possibility that the structure may be methylene-cyclobutenone[5] (VII) instead of the epoxide is excluded by the inertness of (IV) to sodium borohydride in boiling ethanol[6] even when R is the least sterically hindered Me group Furthermore, if structure (VII) is correct, ν(C=O) should appear at a value higher than 1750 cm^{-1}, since it has been shown[7] that the stretching frequency of a strained carbonyl group attached to a four-membered ring is 1780—1750 cm^{-1} For example, cyclobutenedione (VI) and the highly conjugated diketone (VIII) show ν(C=O) in chloroform at 1770 and 1750 cm^{-1}, respectively [2] The epoxide structure was identified finally by acid-catalysed and photochemical epoxide-ring opening, yielding 3-diphenylmethyl-4-halogenodiphenylmethylcyclobutene-1,2-dione (V) in quantitative yields Spectral data of (Va) (crimson plates m p 202—203°) were λ_{max} ($CHCl_3$) 274 (ϵ 30,300), 342 (9500), and 453 nm (13,300), ν_{max} ($CHCl_3$) 1765 (C=O) and 1545 and 1535 cm^{-1} (unsplit doublet, C=C), n m r ($CDCl_3$) τ 2 60 (d, C_6H_5, 10H), 3 13 (d, C_6H_5, 10H), and 4·35 (s, C*H*, 1H) Treatment of (IVa) with DBr in D_2O afforded [Va(D)] which showed no methine proton signal at τ 4·35

The cyclobutenedione (V) absorbs at a much longer wavelength than does 3-phenylcyclobutenedione[8] [λ_{max} ($CHCl_3$) 288 nm (log ϵ 4 40)] On the other hand, the electronic spectrum of (Va) is similar to that of the dibromide (VIa),[2] λ_{max} ($CHCl_3$) 260 (ϵ 20,800), 270 (20,800), 346 (9100), and 460 nm (13,900) Shaking an acetonitrile solution of (Va) with aqueous sodium chloride afforded the same chloro-derivative (Vb) as that derived from (IVb) These data show the existence of conjugation between the phenyl group and the four-membered ring, and suggest that the C–Br bond of (V) and (VI) is not a usual covalent one

Since (IV) was obtained even when the reaction of (I) with sodium alkoxide was carried out in dry alcohol–tetrahydrofuran from which oxygen was removed by evacuation before use, and under a nitrogen atmosphere, the oxygen of the epoxide ring must be derived from an alcohol A possible reaction mechanism is shown in the Scheme It is not unreasonable to consider that the dialkoxy-carbanion (III), produced by the action of alkoxy-anion on the mono-alkoxy-intermediate (II), is converted into (IV) by ring-closure accompanied by 1,3-migration of halogen, since a hydroperoxy-carbanionic intermediate has been suggested[9] for the epoxidation of a double bond with hydrogen peroxide in aqueous alkaline media

The conversion of (IV) into (V) in aqueous acid can be interpreted in terms of three steps, hydrolysis, ketonisation, and double-bond migration.

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